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ScienceDirect

Catalysis Today 130 (2008) 109–116

CATALYSIS TODAY

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Effect of NTA addition on the formation, structure and activity of the active phase of cobalt–molybdenum sulfide hydrotreating catalysts

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Abstract

A series of CoMo alumina catalysts are prepared with constant amount of Co and Mo (2.1 wt.% Co and 10 wt.% Mo) changing the amount of chelating agent nitrilotriacetic acid (NTA) from 0 to 1.2 mol NTA per mole of (Co + Mo). After impregnation, the catalysts are not calcined but directly sulfided before activity test and IR characterization. The activity for thiophene HDS is multiplied by a factor of 2.6 for the highest NTA amounts. IR analysis during sulfidation shows three important domains for decomposition of the NTA complexes: a first one between 463 and 493 K, a second sharp one around 513 K and a final one above 553 K. Adsorption of CO followed by IR spectroscopy shows that the sulfidation of Mo is almost complete at 493 K. The higher promotion level of the NTA-containing catalysts is due to the availability of the Co liberated by decomposition of the NTA complex in the region 463–493 K and above 553 K. From the very good correlation between the HDS activity and the amount of Co-promoted sites, it is concluded that NTA addition affects the concentration of the promoted sites without changing significantly their nature.

Keywords: Chelating agent; NTA; IR spectroscopy; CO; HDS; Hydrotreatment

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1. Introduction

To achieve more stringent regulations in sulfur content for diesel and gasoline, the refiners have to develop more competitive hydrotreatment processes. In order to synthesize highly efficient catalysts, a deep understanding of the relationship between structure and activity has to be reached. The hydrotreating catalysts generally consist of small MoS_2 crystallites promoted by Co (or Ni) well dispersed on an alumina-based support. Several models were proposed for cobalt localization [1–3], but the generally accepted model is the CoMoS one proposed by Topsøe et al. [4–6]. In this model, the Co atoms are anchored on the edges of MoS_2 slabs. Two types of Co–Mo–S were also described: Type I and Type II [7], which are distinguishable by their sulfide state and their active phase-carrier interactions. In addition, the Co atoms can be present in different forms like small cobalt sulfide particles and unsulfided cobalt [8], which are almost inactive.

Many preparation routes were studied in order to improve the amount of Co in the CoMoS state. Among them, addition of a chelating agent was a successful one since, as a general manner, an increase of activity is reported [9–15]. Some discrepancies in the extent of activity increase can be observed. These differences point out the importance of the nature and amount of chelating agent, the nature of metals precursors, the presence or not of a calcination before the sulfidation step, the rate and temperature of the sulfidation. Most of the studies concern the addition of ethylene diamino tetraacetic acid (EDTA), cyclohexane diamine-tetraacetic acid (CydTA) and nitrilotriacetic acid (NTA).

NTA appears as a promising chelating agent. On Mo/Al_2O_3, Hensen et al. [9] reported that the addition of NTA multiplies the rate constant for thiophene HDS by a factor of 1.5. On NTA–$CoMo/Al_2O_3$ catalysts prepared by a “calcination” method, a similar increase of activity was observed by Inamura

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doi:10.1016/j.cattod.2007.07.018

et al. [14]. Kubota et al. [10] prepared NTA–CoW/Al_2O_3 catalysts without calcination and observed an activity multiplied by two compared to that measured on the catalysts prepared without NTA. On a model CoMo catalyst, i.e. CoMo phase deposited on an oxidized Si(1 0 0) wafer, Coulier et al. [11] also observed an improvement of the thiophene HDS activity for the catalyst prepared with NTA. Only Cattaneo et al. [15] observed a decrease of the activity by a factor of 2 on NiMo/Al_2O_3 catalyst after NTA addition.

Different explanations are proposed to account for the beneficial effect of NTA. van Veen et al. [13] deduced from catalytic tests that type II Co–Mo–S phase is selectively formed using NTA. From XPS measurements, Inamura et al. [14] showed that the addition of NTA leads to an increase of the oxidic phase dispersion. Coulier et al. [11] characterized the Mo and Co (Ni) oxidation degrees of model catalysts during the sulfidation stage using XPS analysis. Their results indicate that, on model catalysts, the presence of NTA delays the decomposition of the Co precursor. Consequently, Co atoms remain chelated during molybdenum sulfide slabs formation, which favours Co anchoring on MoS_2 slabs. Hence, literature shows discrepancies regarding the origin of the NTA effect.

In the present work, we studied a set of representative catalysts, i.e. NTA–CoMo catalysts supported on alumina, which contain constant Co and Mo amounts corresponding to the optimum composition usually reported in the literature. The only variation was the amount of NTA present on the catalyst with a molar ratio NTA over metal varying from 0 to 1.2 (0, 0.25, 0.9 and 1.2 mol NTA/mol (Co + Mo)).

The aim of this study was to determine the effect of NTA addition on the formation and activity of the sulfide phase on supported catalysts. The activity of the series of catalysts was tested in HDS of thiophene. Formation of the active phase was characterized (i) by following the decomposition of the precursors through analysis of the gas phase during the sulfidation process and (ii) by using infrared spectroscopy of CO [16,17] to identify and quantify the sites formed on the sulfide phase and on the support at different stages of the sulfidation process.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by incipient wetness impregnation of a γ-alumina ($S_{BET} = 258\ m^2\ g^{-1}$; $V_p = 0.66\ cm^3\ g^{-1}$). The NTA was introduced at the same time as the metallic precursors. Different solutions containing cobalt(II)nitrate ($Co(NO_3)_2 \cdot 6H_2O$, from Merck), ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ from Merck) and NTA ($[C_2H_3O_2]_3N$, from Acros) were prepared in order to obtain catalysts containing 2.1 wt.% Co and 10 wt.% Mo and various amounts of chelating agent (0, 0.25, 0.9 and 1.2 mol of NTA/mol of metal (Co + Mo)). The solution was put in contact with the carrier and strongly shaken. Then the preparation was put on a roller bank during 30 min and dried in flowing air at 393 K during 1 h. Note that before sulfidation, the catalysts were not calcined but only dried at 393 K, in order to keep the chelating agent in its initial form. The catalysts are denoted as CoMox.xxNTA where x.xx is the molar ratio NTA/(Co + Mo).

2.2. Thiophene hydrodesulfurization

Atmospheric-pressure gas phase thiophene HDS measurements were performed in a glass flow reactor. About 20 mg of catalyst was sulfided *in situ* in a H_2S/H_2 (10/90) flow of 30 ml/min, with a heating rate of 3 K/min. The temperature was raised till 623 K and maintained at 623 K for 30 min.

The reaction was carried out at 623 K using a feed (90 ml/min) consisting of 8.0 kPa of thiophene, 91.2 kPa of H_2 and 2.1 kPa of H_2S. After 30 min on stream, the products were analyzed every 20 min during 3 h using a Varian 3900 chromatograph equipped with a flame ionization detector (FID). Reaction rate was calculated from steady state conversion using the relation $r = XF/m$ in which X represents the conversion, F the molar flow rate of thiophene and m is the mass of catalyst which was chosen to obtain X lower than 5%.

Since the weight loss of the catalyst during sulfidation can reach up to 25%, results are calculated taking into account the weight of the catalyst after sulfidation (i.e. after decomposition of chelating agent).

2.3. Infrared analysis of the gas phase

The composition of the gas phase was characterized by IR spectroscopy during the sulfidation of the catalyst up to 643 K with a heating rate of 3 K/min under flow of 30 ml/min of H_2S/H_2 (10/90). After contact with the catalyst, the gas flow was introduced in a gas cell for on-line analysis.

2.4. Infrared spectroscopy of CO adsorbed

Low pressure and low temperature CO adsorption experiments were performed in a glass IR cell under static conditions. About 15 mg (precisely weighted) of catalyst were pressed into the form of a disc (2 cm^2). The catalyst wafer was sulfided *in situ* with a H_2S/H_2 (10/90) gas mixture according to two different procedures.

The standard sulfidation process started by the introduction in the IR cell of 1.33×10^4 Pa of H_2S/H_2 at room temperature. The catalyst was heated up to 543 K with a heating rate of 10 K/min and maintained at this temperature for 30 min. During this dwell, the cell was evacuated under primary vacuum (10^{-4} Pa) and 1.33×10^4 Pa of H_2S/H_2 was added again. Then, the temperature was raised up to 623 K and maintained for 30 min at this temperature. During this dwell at 623 K, the cell was evacuated under primary vacuum and 1.33×10^4 Pa of H_2S/H_2 was added again. The catalyst was kept under H_2S/H_2 at 623 K during 90 min. The catalyst was cooled down at 543 K and evacuated under secondary vacuum (10^{-6} Pa) during 30 min. Before CO introduction, the cell was cooled down with liquid nitrogen under pumping. Then, successive small CO doses were introduced and finally 133 Pa of CO at equilibrium was contacted with the catalyst. Further, the CO was eliminated by evacuation at 298 K.

In another set of experiments, the effect of the sulfidation temperature (T_s) was studied. The sample was sulfided *in situ* with a H_2S/H_2 (10/90) gas mixture, as described above. The sulfidation process started by the introduction in the IR cell of 1.33×10^4 Pa of H_2S/H_2 at room temperature. Then, the sample in contact with H_2S/H_2 was heated at 3 K/min until $T_s = 403$, 463, 493, 553 or 573 K. Afterwards, the temperature was adjusted to 543 K (10 K/min) and then the cell was evacuated under secondary vacuum at 543 K during 30 min (10^{-6} Pa). Note that for all the sulfidation temperatures, the final evacuation step was performed at 543 K.

For all these experiments, spectra were recorded after each addition of CO on a Nicolet Nexus spectrometer equipped with a MCT detector. All the spectra were normalized to 5 mg cm^{-2} of sulfided catalyst.

3. Results and discussion

3.1. HDS activity of the NTA catalysts

Fig. 1 presents the influence of NTA amount on the reaction rates of thiophene HDS for the CoMox.xxNTA catalysts. The HDS activity strongly increases until 0.9 mol of NTA per mol of metal while a higher amount of NTA hardly enhances the HDS activity.

These results point out that addition of NTA has a strong effect on the $CoMo/Al_2O_3$ catalyst since the activity in thiophene HDS can be increased by a factor of 2.6. The HDS activity is maximum for a NTA/Co molar ratio of 3.5 (CoMo0.90NTA). Note that Inamura et al. reported an optimum activity for a lower NTA/Co ratio (NTA/Co = 2) [14].

3.2. Effect of sulfidation temperature on the decomposition of precursors of NTA catalysts

3.2.1. Analysis of the gas phase

In order to characterize the effect of NTA on the formation of the sulfide phase, the decomposition of NTA (and of the other precursors) was followed during the sulfidation process. The composition of the gas phase versus the sulfidation temperature (T_s) was analyzed by IR spectroscopy on the CoMo0.00NTA and CoMo1.20NTA catalysts.

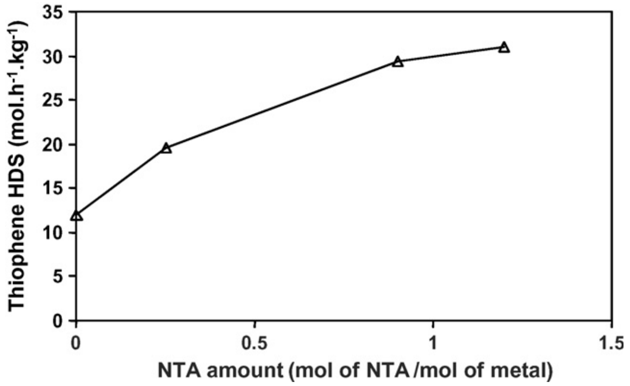

Fig. 1. Thiophene HDS activity of the CoMox.xxNTA/Al_2O_3 catalysts.

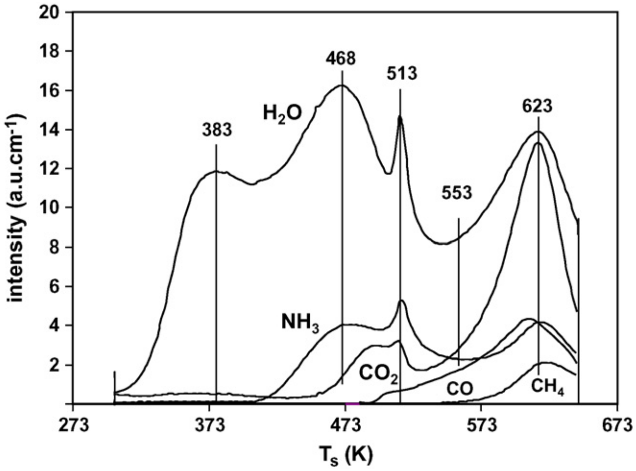

Fig. 2. IR analysis of the gas phase during the sulfidation of CoMo1.20NTA catalyst.

On the CoMo1.20NTA, the formation of different compounds can be observed: H_2O (bands between 1200 and 1800 cm^{-1}), CO_2 (band at 2350 cm^{-1}), CO (band at 2143 cm^{-1}), NH_3 (band at 3330 cm^{-1}), and CH_4 (band at 3016 cm^{-1}). By contrast, for the CoMo0.00NTA catalyst, only water can be detected with the gas cell used for the present study. Fig. 2 reports the area of the bands characteristic of the different products versus sulfidation temperature for CoMo1.20NTA. Note that some uncertainty exists on the CO_2 band area due to the contribution of CO_2 from the spectrometer flush that can slightly vary with time.

From Fig. 2, four main temperature domains can be defined:

- *Zone 293–423 K*: in this temperature domain, only water is detected. The amount of released water reaches its maximum for $T_s = 383$ K. It likely corresponds to the elimination of physisorbed water, which is adsorbed on the catalyst during its storage under air.
- *Zone 423–493 K*: in this domain, H_2O, NH_3 and CO_2 are detected. The maximum for H_2O and NH_3 detection is obtained at 648 K. H_2O formation can be attributed to the dehydroxylation of alumina surface or to the start of MoS_2 phase formation, both processes inducing the release of H_2O. As for CO_2, its formation begins at about 473 K and reaches its maximum at $T_s = 493$ K. The formation of CO_2 and NH_3 reveals that a fraction of the NTA present on CoMo1.20NTA, starts to decompose.
- *Zone 493–553 K*: in this domain, we note the simultaneous appearance of sharp peaks indicating that H_2O, NH_3 and CO_2 are formed in a very narrow temperature domain.
- *Zone 553–623 K*: in this temperature domain, CH_4 and CO are formed in addition to H_2O, NH_3 and CO_2. The maximum of formation of these gases is situated at about 623 K.

Note that some additional products could be formed in the gas phase that are not detected in the IR analysis due to their low concentration or their low molar extinction coefficient.

From the study of the products of decomposition in the gas phase, three zones for decomposition of NTA on NTA–CoMo/

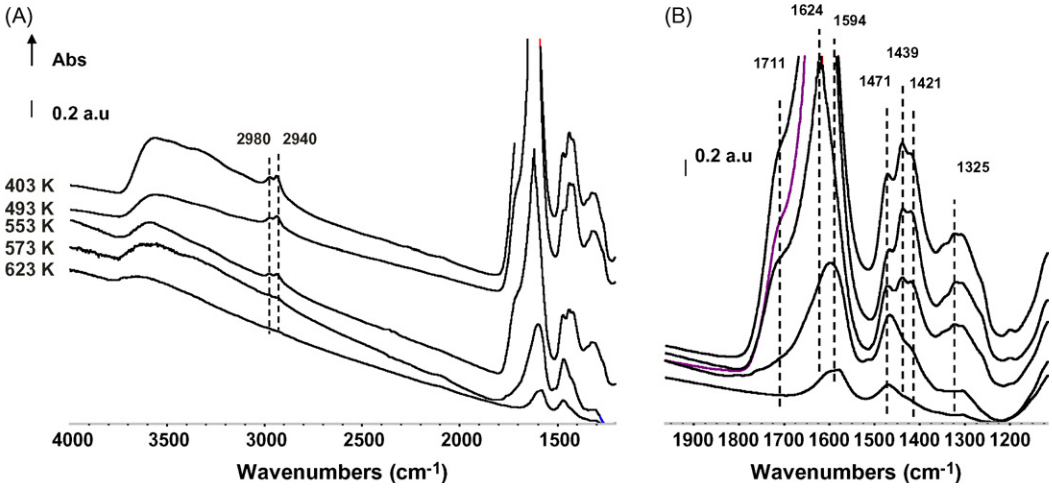

Fig. 3. IR spectra of the CoMo1.20NTA catalyst after sulfidation at $T_s = 403$, 493, 553, 573 and 623 K (A). Same spectra in the zone 1900–1200 $\mathrm{cm^{-1}}$ (B).

Al_2O_3 catalyst can be evidenced. This indicates that the decomposition of NTA occurs in different steps suggesting the formation of different NTA-containing complexes during NTA impregnation and drying.

3.2.2. *Analysis of the surface species*

In order to have a complete view of the NTA catalyst during sulfidation, the surface species present on the CoMo1.20NTA catalyst were characterized after sulfidation at 403, 463 (not shown), 493, 553, 573 and 623 K (Fig. 3). These different temperatures were chosen from the gas phase analysis, as characteristic of the different steps in the NTA decomposition.

Bands in two IR zones can be observed: the zone comprised between 3600 and 2500 $\mathrm{cm^{-1}}$, which is mainly characteristic of the stretching O–H, N–H and C–H bands and that comprised between 1750 and 1200 $\mathrm{cm^{-1}}$, which is mainly representative of the stretching O–C–O, C=O and of the bending C–H bands. In these two zones, the increase of T_s leads to a progressive disappearance of the various bands.

At $T_s = 403$ K, the spectrum presents broad bands between 3200 and 3600 $\mathrm{cm^{-1}}$ indicating the presence of H-bonded water, two ν(C–H) bands at 2980 and 2940 $\mathrm{cm^{-1}}$ and two intense bands at about 1660 and 1430 $\mathrm{cm^{-1}}$ which contain several components. Increase of T_s leads to elimination of H-bonded water and a decrease of the signal of the other species. The increase of the temperature reveals that the envelope at about 1660 $\mathrm{cm^{-1}}$ contains at least two bands at 1711 and 1624 $\mathrm{cm^{-1}}$. The band at 1711 $\mathrm{cm^{-1}}$ should be characteristic of C=O vibrations, while that at 1624 $\mathrm{cm^{-1}}$ indicates the presence of OCO vibrators. These two species progressively disappear with T_s. In the envelope at about 1430 $\mathrm{cm^{-1}}$, numerous bands can be distinguished at 1471, 1439, 1421 and 1325 $\mathrm{cm^{-1}}$ (Fig. 3). The increase of the sulfidation temperature leads to a general decrease of these bands. Some of them are preferentially diminished as those at 1439, 1421 and 1325 $\mathrm{cm^{-1}}$. Bands in this zone can be attributed to the bending CH_2 vibrations and to the symmetric stretching OCO vibrations, which generally give rise to very intense bands. The detection of different bands indicates the formation of different NTA-containing entities. On the spectrum taken after sulfidation at 623 K, only alumina OH groups are detected as well as two bands at 1594 and 1471 $\mathrm{cm^{-1}}$ that can be assigned to carboxylate species, originated from the decomposition of NTA.

In a previous paper, Ryczkowski [18] studied the adsorption of NTA and of its sodium salt on alumina. This author observed that IR spectra of the OCO bands in 1800–1200 $\mathrm{cm^{-1}}$ region are sensitive to the nature of the cation. He also reports that when the complex is deposited on alumina, IR bands are quite different from those of the unsupported compound, which shows that interaction of the chelate molecule with alumina can occur. Hence, our spectra provide evidence for the formation of different NTA-containing complexes on the surface of the catalyst during preparation, which progressively decompose during the sulfidation process. During the preparation, different complexes can be formed like NTA–Co, NTA–Co in interaction with the alumina surface (called NTA–Co–Al), NTA–Mo, NTA–Mo–Al and NTA–Al. In addition, we cannot exclude the presence of some free NTA. Hence, the different complexes that can be formed during preparation of NTA–CoMo/Al_2O_3 catalysts show different stabilities. Results obtained analyzing the gas phase and the adsorbed species show that NTA complexes are still present after sulfidation of CoMo/Al_2O_3 at 573 K.

3.3. *Effect of the sulfidation temperature on the nature and concentration of sulfide phase sites*

3.3.1. *Qualitative analysis*

In order to determine the effect of NTA on the genesis of the sulfide phase sites, CoMo0.00NTA and CoMo1.20NTA were characterized by IR spectroscopy of CO adsorbed at low temperature after sulfidation at 403 (not shown), 463, 493, 553, 573 and 623 K (Fig. 4).

In agreement with previous studies [16], four ν(CO) bands are observed on the sulfided CoMo0.00NTA catalyst (Fig. 4). The bands at 2190 $\mathrm{cm^{-1}}$ (very weak) and 2156 $\mathrm{cm^{-1}}$ are characteristic of CO in interaction with the Al^{3+} CUS and with

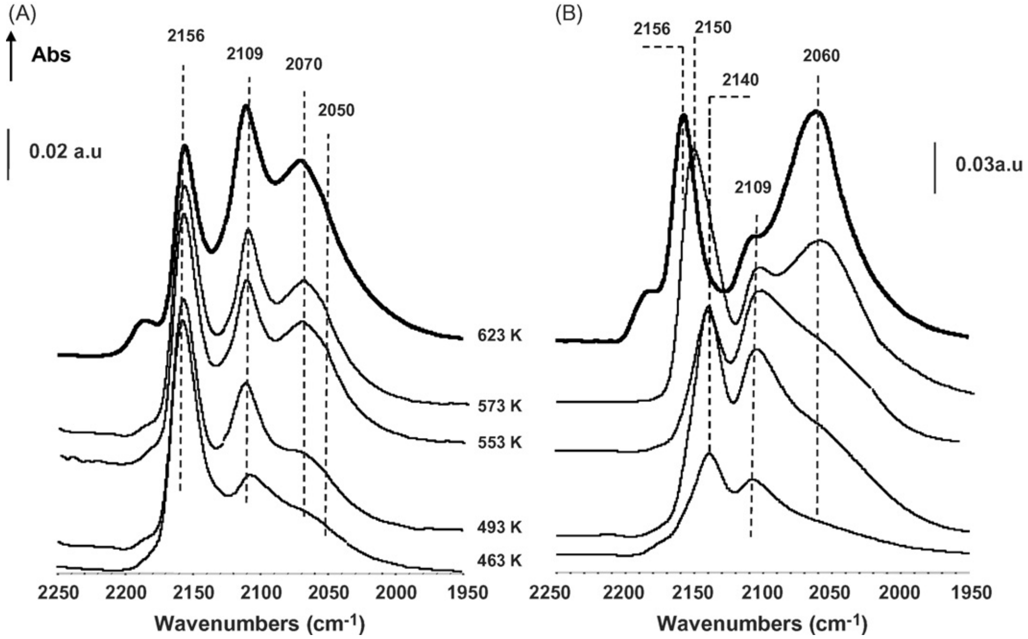

Fig. 4. IR spectra of CO adsorbed on CoMo0.00NTA (A) and on CoMo1.20NTA (B) after sulfidation at $T_s = 463$, 493, 553, 573 and 623 K.

the acidic OH groups of the alumina, respectively. The band at 2109 cm^{-1} is specific of CO adsorbed on unpromoted Mo sites. The band at 2070 cm^{-1}, with a shoulder at 2050 cm^{-1}, corresponds to CO in interaction with the Co-promoted sites (CoMoS sites). These two bands were, respectively, attributed to CO in interaction with the Co sites of the CoMoS phase and with the Mo sites of the CoMoS phase [17]. One can observe that the sulfidation temperature (T_s) has a strong effect on the formation of the sulfide phase. After sulfidation at 403 K, the CO uptake is very small. Sulfidation at $T_s = 463$ K does not significantly increase the CO uptake. By contrast, when T_s is higher than 463 K, CO adsorption on the sulfide phase clearly increases and progressively develops with T_s. Regarding the CO uptake on the support, only small differences arise versus T_s except an important increase of the accessibility of the Al^{3+} sites after sulfidation at 623 K.

On the CoMo1.20NTA catalyst (Fig. 4), the CO band characteristic of the unpromoted Mo sites is detected at 2109 cm^{-1}, i.e. the same wavenumber as in absence of NTA and at 2060 cm^{-1} for the band characteristic Co-promoted sites, i.e. at a slightly lower wavenumber than in absence of NTA. It appears that the presence of NTA strongly modifies the development of the sulfide phase versus T_s.

A special feature of the spectra of the NTA-containing catalyst is the presence of a strong band which maximum shifts from 2140 cm^{-1} up to 2150 and finally up to 2156 cm^{-1} when T_s increases from 403 to 553 and to 623 K. The band at 2140 cm^{-1} is characteristic of physisorbed CO. Its appearance indicates the presence of residual species (see previous section) on the catalyst from incomplete decomposition of the NTA complexes that hinders the interaction between CO and alumina. Increasing the sulfidation temperature from 403 to 493 K leads to an increase in intensity of this band without any shift of the wavenumber. This likely indicates that, at low T_s, the porosity of the catalyst is partially blocked by incomplete decomposition of NTA (and complexes), which limits the formation of the pseudo-liquid CO phase. For $T_s = 553$ K, the maximum of the band is located at 2150 cm^{-1}, a wavenumber comprised between 2140 and 2156 cm^{-1}. This indicates that, at 553 K, the recovery of the accessibility of the alumina surface by a progressive decomposition of NTA residues is limited. At $T_s = 623$ K, the CO spectrum reveals the complete recovery of the accessibility of OH groups as well as of the Lewis acid sites (bands at 2156 and 2195 cm^{-1}, respectively). Note that the intensities of these two bands are very close to that observed for similar T_s on CoMo0.00NTA.

3.3.2. *Quantitative analysis*

To analyze the effect of NTA on the formation of unpromoted and Co-promoted sites with T_s more accurately, the IR spectra were deconvoluted. The broad CO adsorption band characteristic of the sulfide phase was deconvoluted using three Gaussian curves (one for unpromoted sites and two for Co-promoted sites). The concentration of sites was calculated taking into account the area of the bands and the molar extinction coefficients of these bands determined previously ($\varepsilon_{(Mo)} = 16\ \mu mol^{-1}\ cm$; $\varepsilon_{(CoMoS)} = 43\ \mu mol^{-1}\ cm$) [16]. Fig. 5 compares the amount of sites of each type (total, unpromoted and Co-promoted) on CoMo0.00NTA and on CoMo1.20NTA.

Regarding the total concentration of sulfide phase sites (Fig. 5A), it can be observed that, at low temperature of sulfidation, the CO uptake is relatively small both in presence and in absence of NTA. This fact is attributed to the partial sulfidation of the metals at this temperature. The total amount of sites reaches its maximum after a sulfidation at 493 K and stays almost constant for T_s between 493 and 623 K. For T_s comprised between 493 and 623 K, the total concentration of sites is always higher on CoMo1.20NTA than on CoMo0.00NTA.

The variation of the CoMoS site concentration versus sulfidation temperature is presented in Fig. 5B. It can be

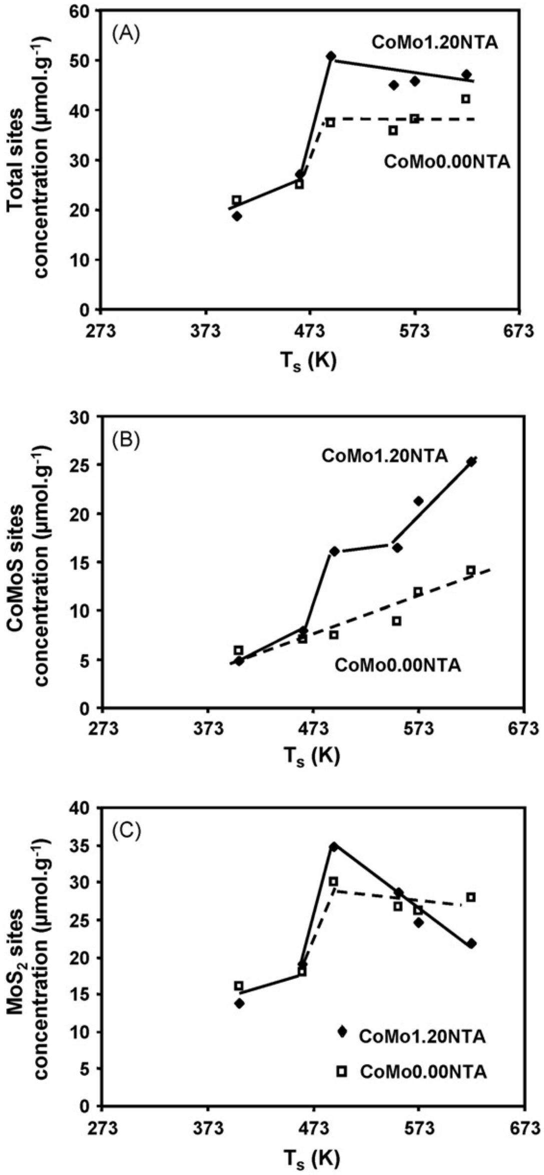

Fig. 5. Variation of the concentration of sites vs. the sulfidation temperature of CoMo0.00NTA and CoMo1.20NTA. (A) Total amount of sulfide phase sites; (B) amount of Co-promoted sites; (C) amount of unpromoted Mo sites.

observed that the CoMoS site concentration increases in parallel on CoMo0.00NTA and CoMo1.20NTA up to $T_s = 463$ K. In absence of NTA, the Co-promoted phase progressively develops with T_s in the whole temperature range (403–623 K). By contrast, in presence of NTA, additional processes occur between $T_s = 463$ and 493 K since a strong increase of the amount of CoMoS sites is observed in this temperature interval. Between 493 and 553 K, their concentration is hardly increased. But, between 553 and 623 K, the amount of created CoMoS sites is greater in presence of NTA than in absence of NTA.

Fig. 5C compares the variation of the concentration of unpromoted Mo sites on the two catalysts. After sulfidation at 403 K, only a small fraction of Mo sites is detected, in agreement with the low sulfidation degree of the catalysts. For the two catalysts, the maximum of Mo sites is detected at 493 K, in both cases followed by a decrease for higher T_s. Note that the concentration of Mo sites decreases more markedly on the CoMo1.20NTA than on the CoMo0.00NTA. These results for the creation of unpromoted Mo sites are in agreement with a previous study on the sulfidation of an unpromoted Mo/Al_2O_3 using a similar method (i.e. effect of T_s on the CO adsorption) [19]. In that work, the CO uptake was very small below 493 K indicating an incomplete sulfidation of the Mo phase. For $T_s = 493$ K, the CO uptake strongly increases and does not change significantly for higher T_s. This indicates that the sulfidation of Mo is complete from $T_s = 493$ K, both on Mo/Al_2O_3 [19] and on CoMo/Al_2O_3 [this work] catalysts. Furthermore, the presence of a chelating agent does not modify the sulfidation behaviour of Mo.

On the NTA-free CoMo catalyst, the amount of Mo sites is almost constant between $T_s = 493$ and 623 K (Fig. 5B), although some Co-promoted sites are created in this T_s range (Fig. 5C). This indicates that the anchoring of Co atoms on MoS_2 edges is compensated by the creation of some Mo sites. On NTA-containing catalyst, the decrease of Mo sites observed for T_s higher than 493 K is in agreement with the important creation of Co-promoted sites. This decrease confirms that, in this T_s range, the creation of Mo sites is moderate conversely to that of promoted sites.

3.4. Effect of the NTA content on the nature and amount of sulfide phase sites

The effect of the amount of NTA on the nature and concentration of sulfide phase sites was studied by CO adsorption after sulfidation of the catalysts at 623 K (Fig. 6). It appears that the NTA content strongly changes the amount of sites of the sulfide phase and affects the acidic properties of the support.

Firstly, increasing the NTA amount (up to 0.9 mol NTA/mol metal) leads to an increase of the interaction of CO with the OH groups whereas the acidity of these OH groups slightly decreases (ν(CO) shifts from 2156 down to 2152 cm^{-1}). For a higher amount of NTA, no significant changes of the intensity and of the frequency are observed compared to the reference catalyst.

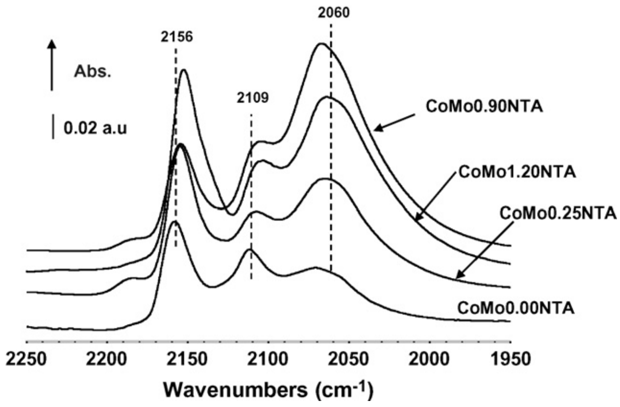

Fig. 6. IR spectra of CO adsorbed on the various NTA catalysts sulfided at 623 K.

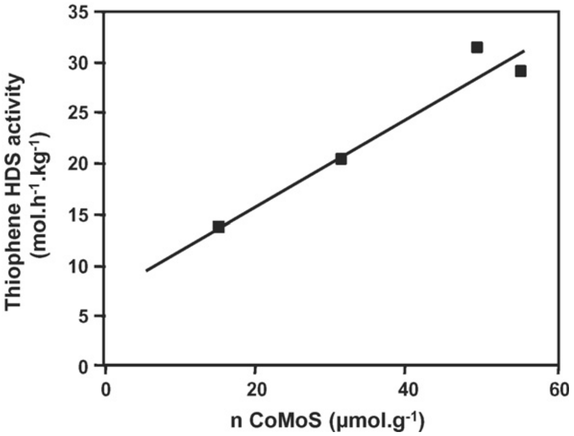

Fig. 7. Comparison between the concentration of CoMoS sites and the thiophene HDS activity.

More important are the changes in the bands characteristic of the sulfide phase. The addition of NTA modifies strongly the concentration of CoMoS sites which is increased by a factor greater than 3. Note that the band intensity is maximum for 0.9 mol NTA/mol metal and decreases for CoMo1.20NTA. Regarding the amount of unpromoted Mo sites, their concentration is not significantly changed taking into account the overlapping between the bands characteristic of Mo and CoMoS sites.

3.5. Structure of the active sites in HDS

Comparison of the thiophene HDS activities with the concentration of CoMoS sites detected by CO is presented in Fig. 7. This figure points out a very good relationship. We can remark that the CoMo0.90NTA and CoMo1.20NTA, which have very similar activities, possess almost the same amount of CoMoS sites. Furthermore, extrapolation to $n(\text{CoMoS}) = 0$ indicates that the activity in absence of CoMoS sites is about 7 mol h^{-1} kg^{-1}, an activity close to that measured on pure Mo catalysts.

This correlation indicates that the Co-promoted sites are responsible for the HDS activity. Moreover, it provides evidence that the activity per site stays constant whatever the NTA amount. This suggests that the structure of Co-promoted sites is not modified by the presence of NTA. Hence, the combination of spectroscopic data and activity test shows that the increase of the HDS activity by NTA addition is not due to a change of the properties of the sites but only to an increase of the concentration of CoMoS sites.

3.6. Effect of NTA on the creation of active sites

The parallel between the effect of the sulfidation temperature on the decomposition of NTA (Figs. 2 and 3) and on the creation of sulfide phase sites (Figs. 4 and 5) presented previously leads to the following remarks:

- Up to $T_s = 463$ K, almost no decomposition of the NTA occurs. Accordingly, no differences are observed in the amount of Mo- and Co-promoted sites formed on the sulfide phase in presence and in absence of NTA. At this stage, the supported phase is mainly in the form of an oxysulfide phase.
- Sulfidation between 463 and 493 K is a key step. During this stage, formation of CO_2 and NH_3 provides evidence for NTA decomposition. In parallel, MoS_2 slabs are formed and comparison with pure Mo catalyst [19] indicates that their formation is almost complete at 493 K. Regarding the CoMoS sites, the amount of Co-promoted sites created on NTA-containing catalyst is clearly greater than on the catalyst without NTA. This fact is in good agreement with the observation of decomposition of the chelating agent.
- Results obtained between 493 and 553 K can be surprising since no significant increase of the amount of Co-promoted sites can be noted on the CoMo-NTA catalyst whereas the gas phase analysis clearly provides evidence for NTA complex decomposition through the detection of CO_2, NH_3 and H_2O in a very narrow temperature zone. Moreover, the formation of these decomposition products cannot be related to the decomposition of NTA in interaction with alumina since in this T_s domain, CO adsorption does not indicate an increase of the accessibility of the support. Thus, the nature of the NTA-complex decomposed in this zone has to be elucidated.
- For higher T_s (553–623 K), NTA continues to decompose as evidenced by the detection of NH_3, CO_2 (in large amounts), and also by the formation of new decomposition products as CO and CH_4. In parallel, Co-promoted sites are created in larger extent than on the NTA-free CoMo catalyst.

Thus, this study points out that the presence of NTA increases the creation of Co-promoted sites specifically between 463 and 493 K and between 553 and 623 K leading to a catalyst that contains a greater amount of CoMoS sites than in absence of NTA.

The presence of NTA does not seem to modify the temperature of formation of the MoS_2 phase, only a small increase of the amount of Mo sites is observed at $T_s = 493$ K. On the NTA catalyst, the decrease of the amount of unpromoted sites, when Co-promoted sites are created, indicates an anchorage of the Co atoms on the MoS_2 edges.

It has to be mentioned that the total amount of sites (Co-promoted + unpromoted Mo sites) is increased by the presence of NTA. Several hypotheses can be proposed to explain this feature such as smaller Mo sulfide slabs, a greater reducibility of the sulfide phase or some differences in the mode of anchorage of the Co atoms on the MoS_2 slabs. Additional experiments will be performed to account for these points that will be presented in a forthcoming paper.

4. Conclusion

NTA addition to CoMo alumina catalysts leads to a significant increase in gas phase thiophene HDS activity. Following the sulfidation processes by IR spectroscopy shows an identical sulfidation process for the creation of the MoS_2 particles in presence and in absence of NTA, i.e. the formation of the MoS_2 slabs is almost complete at 493 K. The Co promotion of the Mo sulfide slabs in absence of NTA is quite low and follows a linear trend with sulfidation temperature up to 623 K. In the presence of NTA, the sulfidation can be divided into several temperature ranges. Between 463 and 493 K and above 553 K, decomposition of chelating agent complex liberates an important quantity of Co, which is available for anchorage on the MoS_2 slabs. The very good correlation between thiophene HDS and the concentration of Co-promoted sites as detected by IR spectroscopy, shows that the main effect of NTA is the increase of the amount of Co-promoted sites without changing significantly the nature of the HDS active sites.

Acknowledgements

MAL thanks the CNRS and the Conseil Régional de Basse Normandie for a grant.

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